



STATUTORY DECLARATION

I, Jun Hee PARK, a citizen of the Republic of Korea and a staff member of Bae, Kim & Lee, specializing in "Semiconductor Devices", do hereby declare that:

1) I am conversant with the English and Korean languages and am a competent translator thereof;

2) To the best of my knowledge and belief, the following is a true and correct translation of the Priority Document (No. KR 1998-63793) in the Korean language already filed with the Korean Intellectual Property Office on December 31, 1998.

Signed this November 3, 2005

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# NOVEL PHOTORESIST CROSS-LINKING COMPOUND, POLYMER THEREOF, AND PHOTORESIST COMPOSITION USING IT

## Field of the Invention

5       The present invention relates to novel photoresist cross-linking monomers, polymers thereof, and photoresist composition using the same. More specifically, it relates to cross-linking monomers for photoresist polymers which can noticeably improve the polymerization ratio of photoresist copolymers, and a process for preparing photoresist copolymers using the same.

## Background of the Invention

10       Recently, chemical amplification-type DUV (deep ultra violet) photoresists have proven to be useful to achieve high sensitivity in processes for preparing micro-circuits in the manufacture of semiconductors. These photoresists are prepared by  
15       blending a photoacid generator with polymer matrix macromolecules having acid labile structures.

20       According to the reaction mechanism of such a photoresist, the photoacid generator generates acid when it is irradiated by the light source, and the main chain or branched chain of the polymer matrix in the exposed portion is reacted with the generated acid to be cross-linked, so that the exposed area is not solved by developing solution, thereby forming a negative image of a mask on the substrate.

      A cross-linker is therefore added to the photoresist to promote cross-linking between the polymers.

25       However, a cross-linking monomer can also be used to promote bonding between the monomers constituting a photoresist polymer, thereby enhancing the yield of the photoresist polymer. For example, when 20 g of monomer is used in the polymerization reaction without using a cross-linker, about 4.8 g of a polymer having molecular weight of about 6,000 is obtained (yield: 24%). When the amount of the

monomer is increased to 40 g, the amount of the polymer obtained is only about 6 g (i.e., the yield is abruptly lowered to about 15%). Thus, in order to prepare photoresist polymer in a large scale, it is desirable to use a cross-linking monomer to increase the yield and make production of the photoresist polymer commercially reasonable.

### **Summary of the Invention**

The object of the present invention is to provide a cross-linking monomer for a photoresist polymer which can noticeably improve the polymerization yield of the photoresist polymer.

Another object of the present invention is to provide a process for preparing a photoresist polymer using said cross-linking monomer, and a photoresist polymer prepared therefrom.

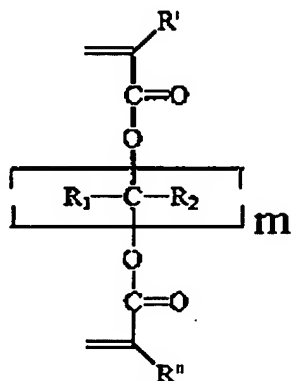
Another object of the present invention is to provide photoresist compositions prepared by using polymers formed from the cross-linking monomer described above.

Still another object of the present invention is to provide a semiconductor element manufactured by using the photoresist composition described above.

### **Detailed Description of the Invention**

To achieve the object described above, the present invention provides a cross-linking monomer represented by the following Chemical Formula 1:

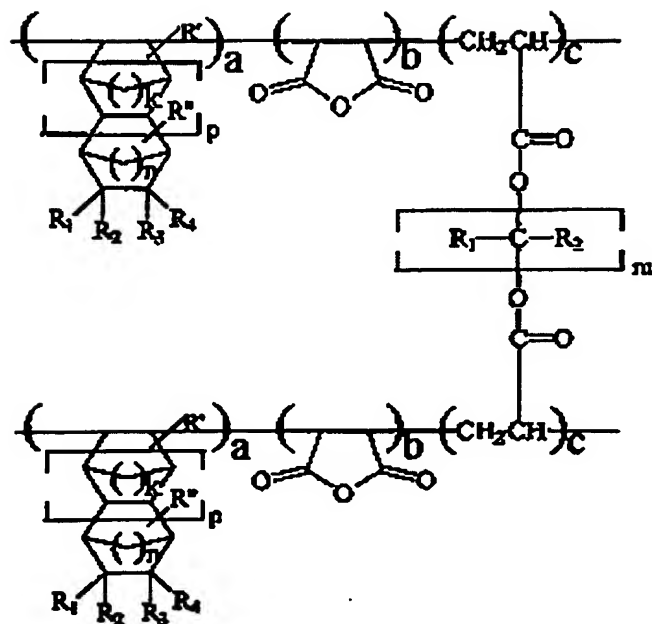
<Chemical Formula 1>



wherein, R' and R'' individually represent hydrogen or methyl; m represents a number from 1 to 10; and R<sub>1</sub> and R<sub>2</sub> are individually selected from the group consisting of hydrogen, straight or branched C<sub>1-10</sub> alkyl, straight or branched C<sub>1-10</sub> ester, straight or branched C<sub>1-10</sub> ketone, straight or branched C<sub>1-10</sub> carboxylic acid, straight or branched C<sub>1-10</sub> acetal, straight or branched C<sub>1-10</sub> alkyl including at least one hydroxyl group, straight or branched C<sub>1-10</sub> ester including at least one hydroxyl group, straight or branched C<sub>1-10</sub> ketone including at least one hydroxyl group, straight or branched C<sub>1-10</sub> carboxylic acid including at least one hydroxyl group, and straight or branched C<sub>1-10</sub> acetal including at least one hydroxyl group.

And, the present invention provides photoresist polymer represented by following Chemical Formula 4:

<Chemical Formula 4>



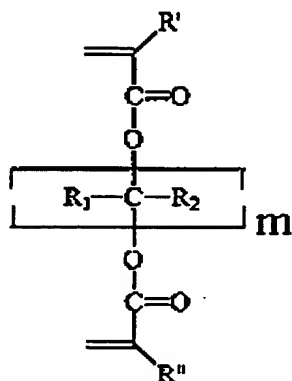
wherein, k and n individually represent the number 1 or 2; m represents a number from 1 to 10; p represents a number from 0 to 5; R' and R'' individually represent hydrogen or methyl; a is polymerization ratio of a conventional photoresist monomer, 1-50 mol%; b is polymerization ratio of a maleic anhydride, 10-50 mol%; c is polymerization ratio of the present photoresist monomer, 0.1-20 mol%; R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are individually selected from the group consisting of hydrogen, straight or branched C<sub>1-10</sub> alkyl, straight or branched C<sub>1-10</sub> ester, straight or branched C<sub>1-10</sub> ketone, straight or branched C<sub>1-10</sub> carboxylic acid, straight or branched C<sub>1-10</sub> acetal, straight or branched C<sub>1-10</sub> alkyl including at least one hydroxyl group, straight or branched C<sub>1-10</sub> ester including at least one hydroxyl group, straight or branched C<sub>1-10</sub> ketone including at least one hydroxyl group, straight or branched C<sub>1-10</sub> carboxylic acid including at least one hydroxyl group, and straight or branched C<sub>1-10</sub> acetal including at least one hydroxyl group.

The present invention is described in more detail hereinafter.

The inventors have performed intensive studies to achieve the objects of the invention described above, and have found that a compound represented by

following Chemical Formula 1 is suitable for photoresist cross-linking monomer.

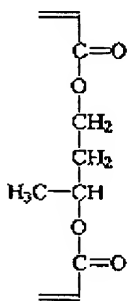
<Chemical Formula 1>



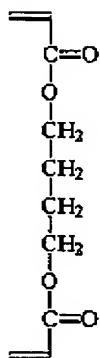
wherein, R' and R'' individually represent hydrogen or methyl; m represents a number from 1 to 10; and R<sub>1</sub> and R<sub>2</sub> are individually selected from the group consisting of hydrogen, straight or branched C<sub>1-10</sub> alkyl, straight or branched C<sub>1-10</sub> ester, straight or branched C<sub>1-10</sub> ketone, straight or branched C<sub>1-10</sub> carboxylic acid, straight or branched C<sub>1-10</sub> acetal, straight or branched C<sub>1-10</sub> alkyl including at least one hydroxyl group, straight or branched C<sub>1-10</sub> ester including at least one hydroxyl group, straight or branched C<sub>1-10</sub> ketone including at least one hydroxyl group, straight or branched C<sub>1-10</sub> carboxylic acid including at least one hydroxyl group, and straight or branched C<sub>1-10</sub> acetal including at least one hydroxyl group.

Preferably, the cross-linking monomer of Chemical Formula 1 is 1,3-butanediol diacrylate represented by Chemical Formula 2 or 1,4-butanediol diacrylate represented by Chemical Formula 3.

<Chemical Formula 2>



<Chemical Formula 3>



The present photoresist cross-linking monomer improves the polymerization yield of polymers by making the photoresist polymers cross-link to one another.

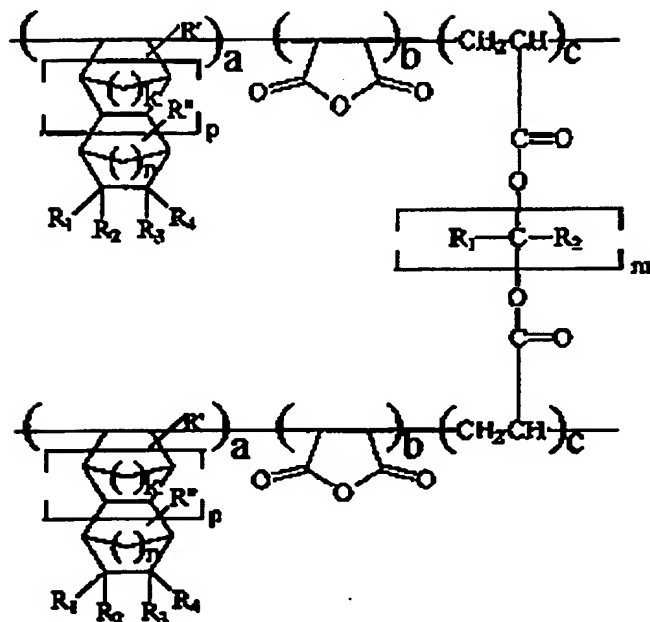
5 The present photoresist cross-linking monomer has two double bonds, and each double bond combines with the other photoresist monomers to form cross-linking, thereby enhancing the polymerization yield of the photoresist polymer.

#### **Preparation of photoresist polymers**

10 The photoresist copolymer can be prepared by dissolving the cross-linking monomers of the present invention with photoresist monomers into the organic solvent.

15 In the case of preparing a photoresist copolymer represented by the following Chemical Formula 4, polymerization is performed by dissolving (bi)cycloalkene derivative (a first monomer), maleic anhydride (a second monomer) and a cross-linking monomer of the present invention in organic solvent, and adding a radical initiator to the resultant solution to induce polymerization:

<Chemical Formula 4>



wherein, k and n individually represent the number 1 or 2; m represents a number from 1 to 10; p represents a number from 0 to 5; R' and R'' individually represent hydrogen or methyl; a is polymerization ratio of a conventional photoresist monomer, 1-50 mol%; b is polymerization ratio of a maleic anhydride, 10-50 mol%; c is polymerization ratio of the present photoresist monomer, 0.1-20 mol%; R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are individually selected from the group consisting of hydrogen, straight or branched C<sub>1-10</sub> alkyl, straight or branched C<sub>1-10</sub> ester, straight or branched C<sub>1-10</sub> ketone, straight or branched C<sub>1-10</sub> carboxylic acid, straight or branched C<sub>1-10</sub> acetal, straight or branched C<sub>1-10</sub> alkyl including at least one hydroxyl group, straight or branched C<sub>1-10</sub> ester including at least one hydroxyl group, straight or branched C<sub>1-10</sub> ketone including at least one hydroxyl group, straight or branched C<sub>1-10</sub> carboxylic acid including at least one hydroxyl group, and straight or branched C<sub>1-10</sub> acetal including at least one hydroxyl group.

The molecular weight of the photoresist polymer represented by Chemical Formula 5 is preferably 3,000 to 100,000.

Bulk polymerization or solution polymerization may be employed as a



polymerization process, and cyclohexanone, methyl ethyl ketone, benzene, toluene, dioxane, tetrahydrofuran, propylene glycol methyl ether acetate and/or dimethylformamide, or mixtures thereof, may be used as a polymerization solvent. As a polymerization initiator, benzoyl peroxide, 2,2'-azobisisobutyronitrile (AIBN),  
5 acetyl peroxide, lauryl peroxide, tert-butyl peracetate, tert-butyl hydroperoxide, di-tert-butyl peroxide, or the like may be used.

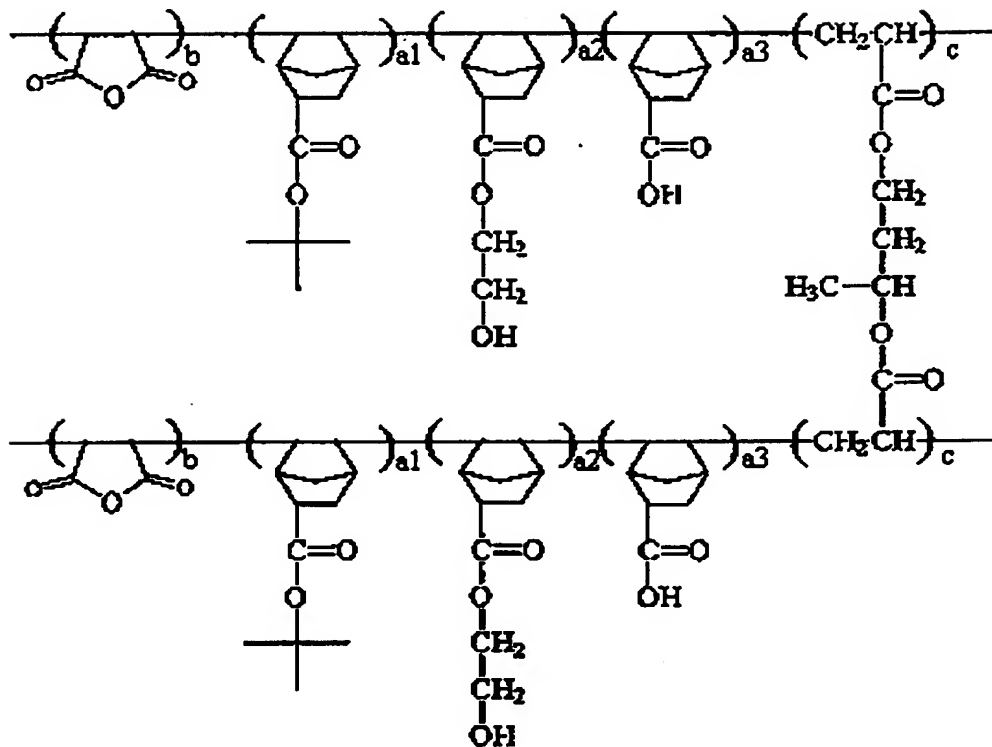
Example 1 : Synthesis of poly(maleic anhydride / 2-hydroxyethyl 5-norbornene-2-carboxylate / tert-butyl 5-norbornene-2-carboxylate / 5-norbornene-2-carboxylic acid / 1,3-butanediol diacrylate)

10

First, (i) 2-hydroxyethyl 5-norbornene-2-carboxylate (0.1 mole), (ii) tert-butyl 5-norbornene-2-carboxylate (0.85 mole), (iii) 5-norbornene-2-carboxylic acid (0.05 mole), (iv) 1,3-butanediol diacrylate (0.1 mole), which is a cross-linking monomer within the scope of Chemical Formula 2, and (v) maleic anhydride (1.0  
15 mole) are dissolved in tetrahydrofuran.

2,2'-azobisisobutyronitrile (AIBN) (6.16g) is added to the resultant solution as a polymerization initiator, and the mixture is reacted at 67°C for 10 hours under an atmosphere of nitrogen or argon. The polymer thus obtained is precipitated from ethyl ether or hexane, and dried to obtain poly(maleic anhydride / 2-hydroxyethyl 5-norbornene-2-carboxylate / tert-butyl 5-norbornene-2-carboxylate / 5-norbornene-2-carboxylic acid / 1,3-butanediol diacrylate) of following Chemical Formula 5 (yield :  
20 35 %):

<Chemical Formula 5>



poly(maleic anhydride / 2-hydroxyethyl 5-norbornene-2-carboxylate / tert-butyl 5-norbornene-2-carboxylate / 5-norbornene-2-carboxylic acid / 1,3-butanediol diacrylate)

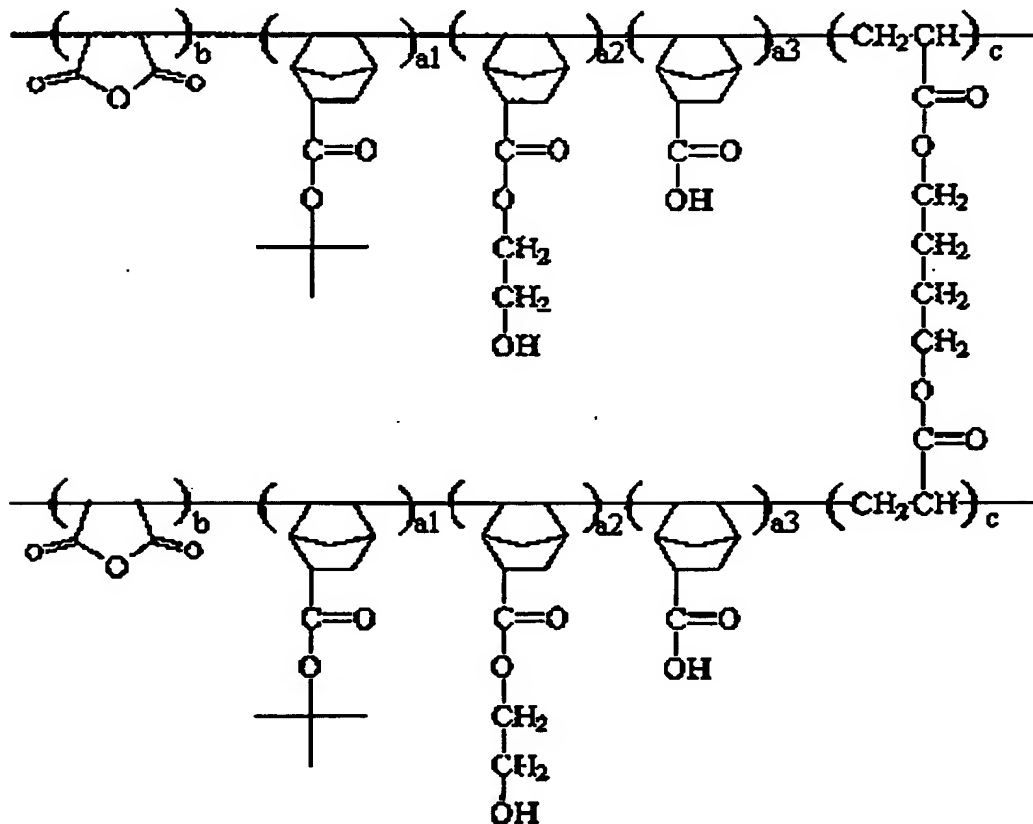
In the above Formula, a1, a2, a3, and b are polymerization ratio of the each monomer, c is polymerization ratio of the present cross-linker. It is preferable that a1 : a2 : a3 : b : c is 0.425 : 0.05 : 0.025 : 0.5 : 0.05.

Example 2 : Synthesis of poly(maleic anhydride / 2-hydroxyethyl 5-norbornene-2-carboxylate / tert-butyl 5-norbornene-2-carboxylate / 5-norbornene-2-carboxylic acid / 1,4-butanediol diacrylate)

The procedure of Example 1 is repeated but using 1,4-butanediol diacrylate instead of 1,3-butanediol diacrylate, to obtain poly(maleic anhydride / 2-

hydroxyethyl 5-norbornene-2-carboxylate / tert-butyl 5-norbornene-2-carboxylate / 5-norbornene-2-carboxylic acid / 1,4-butanediol diacrylate) of following Chemical Formula 6:

<Chemical Formula 6>



5

poly(maleic anhydride / 2-hydroxyethyl 5-norbornene-2-carboxylate / tert-butyl 5-norbornene-2-carboxylate / 5-norbornene-2-carboxylic acid / 1,4-butanediol diacrylate)

10 In the above Formula, a1, a2, a3, and b are polymerization ratio of the each monomer, c is polymerization ratio of the present cross-linker. It is preferable that a1 : a2 : a3 : b : c is 0.425 : 0.05 : 0.025 : 0.5 : 0.05.

The photoresist polymer according to the present invention shows no

significant difference in photolithographic performance from a polymer formed without a cross-linking monomer. However, when the cross-linking monomer of the present invention is employed, the polymerization yield is noticeably increased.

For example, when 20 g of comonomer is employed in the polymerization without using a cross-linking monomer, about 4.8 g of a polymer having molecular weight of about 6,000 is obtained (yield: 24%). When the amount of the comonomer is increased to 40 g, the amount of the polymer obtained is only about 6 g (i.e., the yield is abruptly lowered to about 15% when larger quantities of reactants are used). Thus, merely increasing the quantity of reactants is not a suitable method for producing the copolymer on a large scale.

On the other hand, in the case of performing the same polymerization process using a cross-linking monomer according to the present invention, when 20 g of comonomer is used in the polymerization, about 7 g of the polymer having molecular weight of about 12,000 is obtained (yield: 35%); and, when the amount of the comonomer is increased to 40 g, the amount of the polymer obtained was about 14 g (yield: 35% i.e., no substantial change in the polymerization yield). The molecular weight of the obtained photoresist copolymer was 12,000, and the poly dispersity was about 2.0.

#### **Preparation of photoresist compositions**

The present invention also relates to a photoresist composition containing the cross-linking monomer of the present invention.

A photoresist composition according to the present invention can be prepared by dissolving a photoresist polymer of (i) cross-linking monomer of the present invention and (ii) conventional photoresist monomer into an organic solvent.

Optionally, a small amount of a photoacid generator may also be added to the photoresist composition.

Examples of suitable photoacid generators, including sulfide or onium type

photoacid generators, such as diphenyl iodide hexafluorophosphate, diphenyl iodide hexafluoroarsenate, diphenyl iodide hexafluoroantimonate, diphenyl p-methoxyphenyl triflate, diphenyl p-toluenyl triflate, diphenyl p-isobutylphenyl triflate, diphenyl p-tert-butylphenyl triflate, triphenylsulfonium hexafluorophosphate, triphenylsulfonium hexafluoroarsenate, triphenylsulfonium hexafluoroantimonate, triphenylsulfonium triflate, dibutyl naphthylsulfonium triflate, and the like.

Cyclohexanone, methyl 3-methoxypropionate, ethyl 3-ethoxypropionate, propylene glycol methyl ether acetate, 2-methoxyethyl acetate, 2-heptanone, isobutyl methyl ketone, or the other conventional organic solvents may be used.

#### **Formation of a photoresist pattern**

A photoresist composition prepared according to the present invention may be spin-coated on a silicon wafer to form a thin photoresist film thereon, which is then "soft-baked" in an oven or on a hot plate at 70°C to 200°C, preferably at 80°C to 150°C, for 1 to 5 minutes, and then exposed to patterned light by using a deep ultraviolet exposer or an excimer laser exposer. As the light source, ArF, KrF, E-beam, X-ray, EUV (extremely ultraviolet), DUV (deep ultraviolet) or the like may also be used, and the energy of light exposure is preferably from 1 to 100 mJ/cm<sup>2</sup>.

Then, the thin photoresist film is "post-baked" at 10° to 200°C, preferably at 100°C to 200°C, and the resultant material is impregnated with 2.38wt% or 2.5wt% aqueous TMAH developing solution for a predetermined time, preferably for 40 seconds, to obtain an ultramicro pattern.

A semiconductor element with high integrity can be manufactured by using the photoresist pattern according to the present invention.

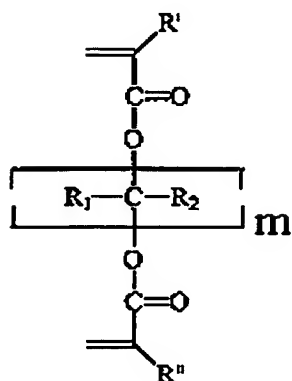
The above description discloses only certain embodiments related to processes for preparing a photoresist copolymer or a photoresist composition by using a cross-linking monomer. It should be understood that the present invention is not restricted to these examples, but includes using the cross-linking monomer of the

present invention in any process for producing a conventional photoresist copolymer or photoresist composition.

**What is claimed is:**

1. A compound for a photoresist cross-linking monomer represented by following Chemical Formula 1:

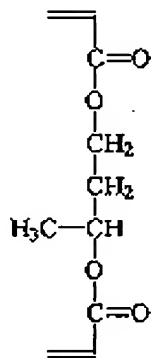
<Chemical Formula 1>



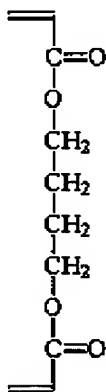
wherein, R' and R'' individually represent hydrogen or methyl; m represents a number from 1 to 10; and R<sub>1</sub> and R<sub>2</sub> are individually selected from the group consisting of hydrogen, straight or branched C<sub>1-10</sub> alkyl, straight or branched C<sub>1-10</sub> ester, straight or branched C<sub>1-10</sub> ketone, straight or branched C<sub>1-10</sub> carboxylic acid, straight or branched C<sub>1-10</sub> acetal, straight or branched C<sub>1-10</sub> alkyl including at least one hydroxyl group, straight or branched C<sub>1-10</sub> ester including at least one hydroxyl group, straight or branched C<sub>1-10</sub> ketone including at least one hydroxyl group, straight or branched C<sub>1-10</sub> carboxylic acid including at least one hydroxyl group, and straight or branched C<sub>1-10</sub> acetal including at least one hydroxyl group.

2. A compound according to claim 1 selected from the group consisting of compounds represented by the following Chemical Formula 2 and Chemical Formula 3:

<Chemical Formula 2>



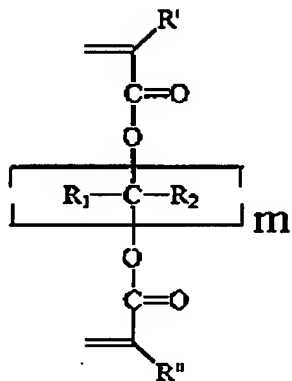
<Chemical Formula 3>



- 5 3. A photoresist polymer comprising the polymerization product of (i) a cross-linking monomer represented by following Chemical Formula 1 and (ii) two or more photoresist monomer.



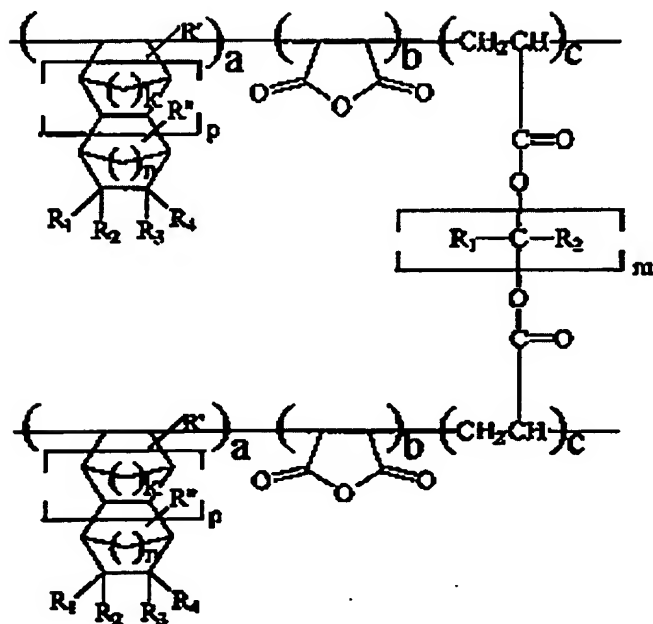
<Chemical Formula 1>



wherein, R' and R'' individually represent hydrogen or methyl; m represents a number from 1 to 10; and R<sub>1</sub> and R<sub>2</sub> are individually selected from the group consisting of hydrogen, straight or branched C<sub>1-10</sub> alkyl, straight or branched C<sub>1-10</sub> ester, straight or branched C<sub>1-10</sub> ketone, straight or branched C<sub>1-10</sub> carboxylic acid, straight or branched C<sub>1-10</sub> acetal, straight or branched C<sub>1-10</sub> alkyl including at least one hydroxyl group, straight or branched C<sub>1-10</sub> ester including at least one hydroxyl group, straight or branched C<sub>1-10</sub> ketone including at least one hydroxyl group, straight or branched C<sub>1-10</sub> carboxylic acid including at least one hydroxyl group, and straight or branched C<sub>1-10</sub> acetal including at least one hydroxyl group.

4. A photoresist polymer according to claim 3, wherein the polymer is represented by the following Chemical Formula 4:

<Chemical Formula 4>



wherein, k and n individually represent the number 1 or 2; m represents a number from 1 to 10; p represents a number from 0 to 5; R' and R'' individually represent hydrogen or methyl; a is polymerization ratio of a conventional photoresist monomer, 1-50 mol%; b is polymerization ratio of a maleic anhydride, 10-50 mol%; c is polymerization ratio of the present photoresist monomer, 0.1-20 mol%; R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are individually selected from the group consisting of hydrogen, straight or branched C<sub>1-10</sub> alkyl, straight or branched C<sub>1-10</sub> ester, straight or branched C<sub>1-10</sub> ketone, straight or branched C<sub>1-10</sub> carboxylic acid, straight or branched C<sub>1-10</sub> acetal, straight or branched C<sub>1-10</sub> alkyl including at least one hydroxyl group, straight or branched C<sub>1-10</sub> ester including at least one hydroxyl group, straight or branched C<sub>1-10</sub> ketone including at least one hydroxyl group, straight or branched C<sub>1-10</sub> carboxylic acid including at least one hydroxyl group, and straight or branched C<sub>1-10</sub> acetal including at least one hydroxyl group.

5. A photoresist copolymer according to claim 4, wherein a, polymerization ratio of the conventional photoresist monomer, is 1 to 50 mol%, b, polymerization

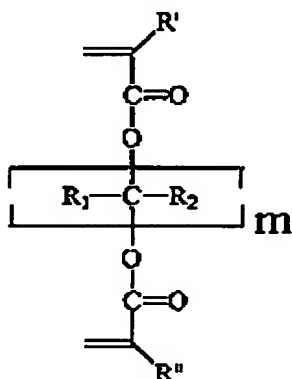
ratio of maleic anhydride, is 10 to 50 mol%, and c, polymerization ratio of the present photoresist cross-linking monomer, is 0.1 to 20 mol%.

6. A photoresist copolymer according to claim 4 comprising poly(maleic anhydride / 2-hydroxyethyl 5-norbornene-2-carboxylate / tert-butyl 5-norbornene-2-carboxylate / 5-norbornene-2-carboxylic acid / 1,3-butanediol diacrylate); or  
5 poly(maleic anhydride / 2-hydroxyethyl 5-norbornene-2-carboxylate / tert-butyl 5-norbornene-2-carboxylate / 5-norbornene-2-carboxylic acid / 1,4-butanediol diacrylate).
7. A photoresist composition comprising (i) a photoresist polymer comprising the  
10 polymerization product of cross-linking monomer represented by Chemical Formula of claim 1 and two or more photoresist monomer, and (ii) an organic solvent.
8. A photoresist composition according to claim 7, which further comprises a photoacid generator.
- 15 9. A process for forming a photoresist pattern, which comprises the steps of (a) coating a photoresist composition according to claim 7 on a wafer, (b) exposing the wafer to patterned light by employing an exposers, and (c) developing the exposed wafer.
- 20 10. A process for forming a photoresist pattern according to claim 9, wherein the light source of the exposers is selected from the group consisting of ArF, KrF, E-beam, X-ray, EUV (extremely ultraviolet) and DUV (deep ultraviolet).
11. A semiconductor element manufactured by using a process according to claim 9.

## ABSTRACT

The present invention relates to a cross-linking monomer, polymer thereof and photoresist composition using it. More specifically, the present invention relates to a cross-linking monomer which can noticeably improve the polymerization ratio of photoresist polymers, a photoresist polymers and a photoresist composition using the same. The present invention discloses a cross-linking monomer represented by the following Chemical Formula 1, and a photoresist polymer using the same.

<Chemical Formula 1>



wherein, R' and R'' individually represent hydrogen or methyl; m represents a number from 1 to 10; and R<sub>1</sub> and R<sub>2</sub> are individually selected from the group consisting of hydrogen, straight or branched C<sub>1-10</sub> alkyl, straight or branched C<sub>1-10</sub> ester, straight or branched C<sub>1-10</sub> ketone, straight or branched C<sub>1-10</sub> carboxylic acid, straight or branched C<sub>1-10</sub> acetal, straight or branched C<sub>1-10</sub> alkyl including at least one hydroxyl group, straight or branched C<sub>1-10</sub> ester including at least one hydroxyl group, straight or branched C<sub>1-10</sub> ketone including at least one hydroxyl group, straight or branched C<sub>1-10</sub> carboxylic acid including at least one hydroxyl group, and straight or branched C<sub>1-10</sub> acetal including at least one hydroxyl group.